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Thickness scaling of the space-charge-limited current in poly(*p*-phenylene vinylene)

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Charge transport in light-emitting diodes (LEDs) based on a poly(*p*-phenylene vinylene) (PPV) derivative is investigated as a function of sample thickness. Via the thickness dependence, the contributions from the electric field and charge carrier density to the mobility in space-charge-limited (SCL) diodes can be disentangled. It is demonstrated that a field-dependent mobility weakens the thickness dependence of the SCL current, whereas a carrier-density-dependent mobility gives rise to an enhanced thickness dependence. The enhanced thickness dependence of the experimental SCL current in PPV is in agreement with the predictions using a density-dependent mobility only. This observation confirms that in PPV-based LEDs, the hole transport is dominated by filling of the localized states. © 2005 American Institute of Physics. [DOI: 10.1063/1.1868865]

Since electroluminescence was reported more than one decade ago, poly(*p*-phenylene vinylene) (PPV) has become one of the most used semiconductors in light-emitting diodes (LEDs).^{1,2} The charge transport properties have been extensively studied in order to understand the fundamental phenomena that govern the operation of these devices.^{3,4} The current through polymer LEDs based on PPV derivatives is space-charge limited (SCL) with a constant hole mobility (μ_h) at low bias voltages at room temperature. At high bias voltages the enhancement of the SCL current has been attributed to a field-dependent mobility of the form⁴

$$\mu_h(E, T) = \mu_h(0, T) \exp(\gamma(T) \sqrt{E}), \quad (1)$$

with $\mu_h(0, T)$ the hole mobility at zero field and $\gamma(T)$ the field activation factor, which reflects the lowering of the hopping barriers in the direction of the applied electric field. Recently, also the dependence of the hole mobility μ_h on the carrier density in a PPV derivative has been investigated by a combined study on polymeric diodes and field-effect transistors (FETs).⁵ It has been demonstrated that the hole mobility is constant for charge carrier densities typically $< 10^{22} \text{ m}^{-3}$ and increases with a power law with density for carrier densities $> 10^{22} \text{ m}^{-3}$. This power-law increase is described by a variable range hopping model in an exponential density of states with energy width kT_0 .⁶ Combination of the diode and field-effect measurements shows that around room temperature, the dependence of the hole mobility on charge carrier density is given by the empirical relation⁵

$$\mu_h(p, T) = \mu_h(0, T) + \frac{\sigma_0}{e} \left(\frac{\left(\frac{T_0}{T}\right)^4 \sin\left(\pi \frac{T}{T_0}\right)}{(2\alpha)^3 B_c} \right)^{T_0/T} p^{T_0/T-1}, \quad (2)$$

where $\mu_h(0, T)$ is the hole mobility at low densities obtained from the quadratic SCL current, σ_0 is a prefactor for the

conductivity, α^{-1} is the effective overlap parameter between localized states, T_0 is a measure of the width of the exponential density of states, and $B_c = 2.8$ is the critical number for the onset of percolation. The parameters σ_0 , α^{-1} , and T_0 are obtained from the temperature dependence of the transfer characteristics of the FET.⁵

In a SCL device, an increase of the applied bias voltage gives rise to a simultaneous increase of the electric field and charge carrier density. Consequently, it is not trivial to disentangle the contributions of the charge carrier density and the electric field to the mobility from a SCL current. We have recently shown that the SCL current in OC₁C₁₀-PPV cannot only be described using a field-dependent mobility (Eq. (1)), but that also a combination of Eq. (2) with the SCL model provides a good description of the hole current.⁷ It should be noted that when applying Eq. (1), the field-enhancement parameter γ is used as a fit parameter to describe the SCL current. In contrast, the calculated SCL current based on Eq. (2) is not a fit, since all parameters are known from field-effect measurements. The good agreement with the experimental data is therefore a strong indication that at room temperature the charge carrier density dependence of the mobility dominates the charge transport. In numerous experimental and model studies of LEDs, the possible role of this effect was not considered.^{4,8-10} In the present study we have investigated the thickness dependence of the SCL current, which can be used to discriminate the effect of a field from that of density-dependent mobility. The enhanced thickness dependence of the experimental SCL current provides a direct proof that the carrier-density-dependent mobility dominates the hole transport in PPV-based diodes.

The polymer used for the present study is the PPV derivative poly[{2-(4-(3',7'-dimethyloctyloxyphenyl))}-co-{2-methoxy-5-(3',7'-dimethyloctyloxy)}-1,4-phenylene vinylene] (NRS-PPV). The chemical structure of the polymer is presented in the inset of Fig. 1. Hole-only diodes from this NRS-PPV are prepared as follows. On top of a glass substrate, a transparent electrode, indium tin oxide (ITO) has been patterned to form the hole-injecting electrode. On top

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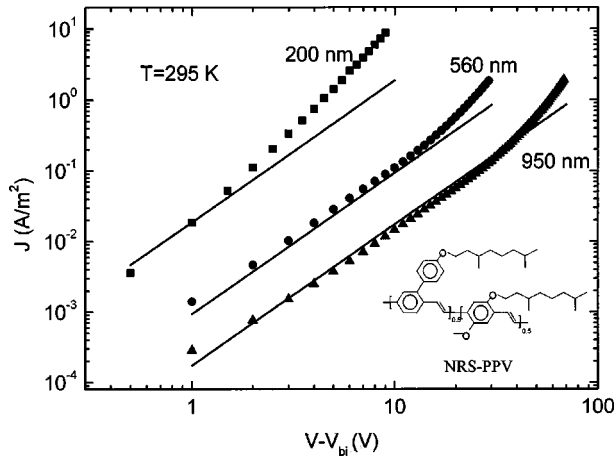


FIG. 1. Room-temperature current density vs voltage characteristics of NRS-PPV hole-only diodes with thicknesses of 200, 560, and 950 nm. The solid lines represent the prediction from the SCL model using a constant hole mobility of $5.0 \times 10^{-12} \text{ m}^2/\text{V s}$ [(Eq. (3))].

of the ITO, a 100–1000 nm polymer film has been spin coated from toluene solution. The device was finished by thermal evaporation of silver (Ag) through a shadow mask. The hole-only diodes have been measured under a controlled N_2 atmosphere. The electrical measurements have been performed using a Keithley 2400 SourceMeter.

In Fig. 1 the current density-voltage (J - V) measurements are presented for NRS-PPV hole-only diodes with thicknesses L of 200, 560, and 950 nm. The applied voltage is corrected for the built-in voltage V_{bi} of 1 V resulting from the work function difference between ITO and Ag. As a first step, we check whether the experimental current at low voltages obeys the conventional Mott–Gurney (MG) law given by⁴

$$J_{\text{MG}} = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu_h(0, T) \frac{V^2}{L^3}, \quad (3)$$

with $\varepsilon_0 \varepsilon_r$ the dielectric constant, as indicated by the solid lines in Fig. 1. The observed occurrence of a SCL current enables a direct determination of the hole mobility for NRS-PPV at low voltages, which is $5.0 \times 10^{-12} \text{ m}^2/\text{V s}$. For low voltages, the mobility is constant and independent of electric field and charge carrier density. At higher voltages it is observed, as before in OC₁₀-PPV,⁴ that the current increase is more steep than a quadratic relation with the voltage. The question is now whether this increase stems from the field dependence of the mobility (Eq. (1)) or from the density dependence (Eq. (2)), which are both enhanced with increasing voltage. For a field-dependent mobility $\mu_h(E)$ of the form of Eq. (1), it has been demonstrated that the SCL current can be approximated by¹¹

$$J = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu_h(E=0) \exp\left(0.89 \gamma \sqrt{\frac{V}{L}}\right) \frac{V^2}{L^3}. \quad (4)$$

For a large field-enhancement factor γ the exponential factor will dominate the increase of the current. As a result, $V(L)$ curves at a fixed current density fall in between the curves $V = V_0(L/L_0)$ and $V = V_0(L/L_0)^{3/2}$, depending on the magnitude of γ . Here V_0 is the voltage at a certain reference thickness L_0 , at the chosen fixed current density. In other words, the increase of the voltage with increasing thickness, at a fixed current density, is *smaller* than would be expected on

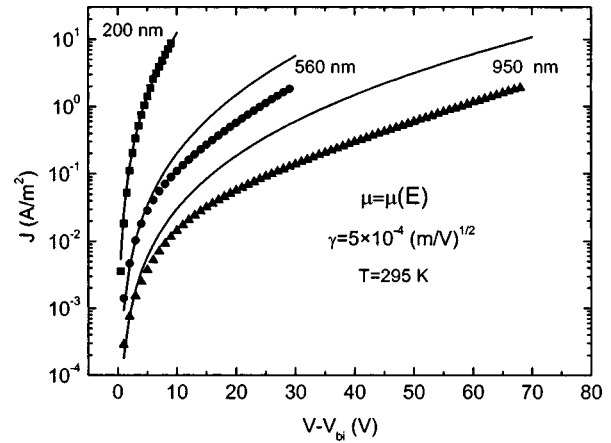


FIG. 2. Room-temperature current density vs voltage characteristics of NRS-PPV hole-only diodes with thicknesses of 200, 560, and 950 nm, respectively. The solid lines represent the prediction from the SCL model combined with a field-dependent mobility [Eq. (1)] The field enhancement factor amounts to $5 \times 10^{-4} (\text{m/V})^{1/2}$.

the basis of Eq. (3). On the other hand, for a density-dependent mobility $\mu_h(p)$ according to Eq. (2), we have recently demonstrated that it can be approximated by $J = 0.8 e p_{\text{av}} \mu_h(p_{\text{av}}) E_{\text{av}}$,⁷ with $E_{\text{av}} = V/L$, p_{av} the average density in the device given by $p_{\text{av}} = (3/2)(\varepsilon_0 \varepsilon_r V / e L^2)$,¹² and $\mu_h(p_{\text{av}})$ the mobility at density p_{av} . Combining this equation with Eq. (2) leads to a thickness dependence of the form

$$J = J_{\text{MG}} + c \frac{V}{L^2} \cdot \left(\frac{V}{L^2}\right)^{T_0/T-1} \cdot \frac{V}{L} = J_{\text{MG}} + c \frac{V^{T_0/T+1}}{L^{2(T_0/T)+1}}, \quad (5)$$

where c is a proportionality constant. For $T_0 = T$ this will lead to the conventional V^2/L^3 behavior. For the materials of interest, T_0 is well above room temperature.⁵ For $T_0 \gg T$ and sufficiently large voltages, where the second term is much larger than J_{MG} , the thickness dependence will approach a V/L^2 scaling. In other words, the increase of the voltage with increasing thickness, at a fixed current density, is in this case *larger* than would be expected on the basis of Eq. (3). In conclusion, the conventional V^2/L^3 scaling will be weakened by a field-dependent mobility (V/L) and enhanced by a density-dependent mobility (V/L^2). Consequently, the thickness dependence of the SCL current at high voltages can be used to discriminate between the contributions from field and charge carrier density.

In order to exactly model the SCL currents with either $\mu_h(E)$ or $\mu_h(p)$, Eqs. (1) and (2) are combined with¹²

$$J = p(x) e \mu_h[p(x), E(x)] E(x), \quad (6)$$

$$\frac{\varepsilon_0 \varepsilon_r}{e} \frac{dE(x)}{dx} = p(x), \quad (7)$$

$$V = \int_0^L E(x) dx, \quad (8)$$

with $p(x)$ the density of holes, and $E(x)$ the electric field. These equations are solved numerically for a given hole current density J . In Fig. 2 the experimental J - V characteristics are shown together with the numerical model calculations using a field-dependent mobility only. As a reference, the 200 nm device is fitted to determine the field-enhancement factor γ of $5 \times 10^{-4} (\text{m/V})^{1/2}$, close to earlier results on

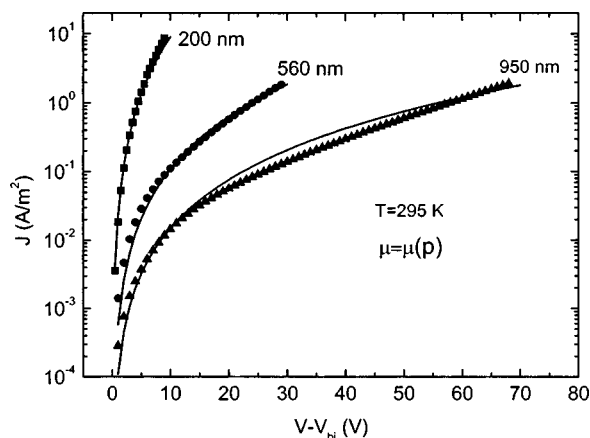


FIG. 3. Room-temperature current density vs voltage characteristics of NRS-PPV hole-only diodes with thicknesses of 200, 560, and 950 nm, respectively. The solid lines represent the prediction from the SCL model combined with a density-dependent mobility [Eq. (2)]. The mobility parameters amount to $\sigma_0 = 3.5 \times 10^6$ S/m, $\alpha^{-1} = 1.36$ Å, and $T_0 = 560$ K, as obtained from field-effect measurements.

OC₁C₁₀-PPV.⁴ This γ value is then used to predict the SCL currents for the thicknesses of the 560 and 950 nm devices. As shown in Fig. 2, the predicted currents (solid lines) clearly overestimate the SCL currents at high voltages. Apparently, the calculated thickness dependence using $\mu_h(E)$ is too weak. Fitting the experimental data would lead to γ values of 3×10^{-4} (m/V)^{1/2} and 2×10^{-4} (m/V)^{1/2} for the 560 and 950 nm devices, respectively. A thickness-dependent γ is, of course, not physical.

In a recent study, the transfer characteristics of NRS-PPV-based FETs have been investigated.¹³ From the temperature dependence, the following parameters for NRS-PPV have been determined: $\sigma_0 = 3.5 \times 10^6$ S/m, $\alpha^{-1} = 1.36$ Å, and $T_0 = 560$ K. The numerically calculated SCL currents using the density-dependent mobility with these parameters in Eq. (2) are shown in Fig. 3, together with the experimental data. It appears that the predicted SCL currents using $\mu_h(p)$ are in good agreement with the experimental SCL current for the whole thickness range studied. Note that the calculated currents do not contain any fit parameter. This result demonstrates that the experimental J - V characteristics indeed exhibit the enhanced thickness dependence, as expected from the density-dependent mobility. This observation is therefore a clear proof of the dominance of a density-dependent mobility in the current in polymeric LEDs. The injected charges will first occupy the energetically lowest localized states of the organic semiconductor. With increasing voltage, the additional charges in the SCL diode fill up higher states and therefore will need less activation energy for hops towards neighboring sites. As a result, the charge carrier mobility will be enhanced at higher voltages. The fundamental question as

to whether the increase of the mobility in a SCL device is dominated by either the carrier density or the electric field is relevant for the operation of LEDs, because these two effects lead to a different electric field and carrier density distribution across the device, affecting the position-dependent recombination probability.⁷ The present results show that for PPV-based diodes at room temperature, the density contribution is very significant and cannot be neglected, as it has been so far in the description of the charge transport in these devices. In general, the dominance of either carrier density or electric field will be a complex function of temperature, applied voltage, device geometry, and amount of disorder in the polymer. A theoretical model has recently been developed to disentangle all these effects.¹⁴

In conclusion, we have investigated the hole transport in NRS-PPV hole-only diodes as function of sample thickness. The SCL current in hole-only diodes can be governed by both the dependence of the hole mobility on the electric field and the charge carrier density. The thickness dependence enables us to discriminate between the two contributions. The experimentally obtained enhanced thickness dependence demonstrates that, for these polymeric LEDs at room temperature, the deviation of the SCL current at high voltages from the Mott-Gurney law is predominantly due to the dependence of the mobility on the carrier density.

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